

PATENT SPECIFICATION

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(54) BLOCK OR GRAFT COPOLYMERS OF POLYALKYLENE OXIDES AND VINYL-AROMATIC OR DIENE POLYMERS

(71) We, BASF AKTIENGESellschaft, a German Joint Stock Company of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pay that a Patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following Statement:—

This invention relates to block or graft copolymers containing one or more polyalkylene oxide blocks A and one or more vinylaromatic polymer and/or diene polymer blocks B, and it further relates to a process for the manufacture of said block copolymers.

It is well known that diene hydrocarbons may be polymerized in non-polar solvents using organolithium initiators to form polydienes of low 1,2-vinyl content (cf. for example German Published Application 1,087,809).

It is also known that alkylene oxides may be polymerized in polar solvents using organometallic compounds of sodium or potassium.

Block copolymers of diene polymers and polyalkylene oxides may be simply made by polymerizing a diolefin with organometallic compounds of sodium or potassium in polar solvents followed by the addition of alkylene oxide. However, in such block copolymers the diene polymer block generally has 1,2-vinyl contents of from 65 to 80%. Thus the block copolymers have high glass temperatures and show only limited elastomeric characteristics.

When the attempt is made to add ethylene oxide to polybutadienyl lithium which has been prepared in non-polar solvents, only one ethylene oxide unit is added with chain termination without block copolymers being formed.

The present invention seeks to provide block copolymers of diene polymers and polyalkylene oxides, which block copo-

lymers have a low 1,2-vinyl content in the diene polymer blocks and thus have a low glass temperature.

It also seeks to provide a general process for the manufacture of a block or graft copolymer of one or more polyalkylene oxide blocks and one or more vinylaromatic polymer and/or diene polymer blocks.

According to the present invention there is provided a process for the manufacture of a block or graft copolymer of one or more polyalkylene oxide blocks and one or more vinylaromatic polymers and/or diene polymer blocks, in which

- (a) one or more vinylaromatic monomers and/or diene monomers are polymerized in a non-polar hydrocarbon solvent to form a block B using an organolithium compound as initiator,
- (b) methyl methacrylate is added to the living chain ends of the polymer block B in amounts of from 0.5 to 10% by weight of said block B,
- (c) a polymer block A is separately made by homopolymerization of one or more alkylene oxides or block copolymerization of one or more alkylene oxides with one or more vinylaromatic monomers and/or diene monomers using an organosodium or organopotassium compound as initiator in an organic solvent which is preferably polar and
- (d) block A is finally added to block B with the reaction of at least one living alkali metal alcoholate end group of block A with at least one ester group of block B with the elimination of alkali metal methoxide.

This process is particularly suitable for making block copolymers of the formula BA or BAB, where A is a polyalkylene oxide block and B is a diene polymer block, wherein less than 60% and preferably less than 15% of the diene units have 1,2-vinyl

structure, the blocks being linked by one or more methyl methacrylate units.

In stage (a) of the process, polymerization of one or more diene monomers and/or vinylaromatic monomers may be carried out in a conventional manner using an organolithium catalyst in a non-polar hydrocarbon solvent. The monomers used are vinylaromatic compounds such as styrene or nuclear substituted or side-chain substituted styrenes, the term "vinyl" thus including vinylidene compounds, and dienes such as butadiene and isoprene. The monomers may be polymerized alone or in admixture with each other. Alternatively, one monomer may be homopolymerized and a further monomer then added to the resulting living polymer.

The polymerization is carried out in a non-polar hydrocarbon solvent, preferably an aromatic hydrocarbon such as benzene, toluene or ethyl benzene. The monomer(s) should preferably be present in solution in a total concentration of from 5 to 50% by weight of the total solution. With the use of a non-polar solvent as the sole solvent, the resulting diolefin blocks contain less than 15% of 1,2-vinyl units. By controlled addition of a polar solvent such as an ether or amine in an amount of up to 10% by weight of the total solution it is possible to raise the content of 1,2-vinyl units up to 60%.

The initiator used is an organolithium compound, preferably *n*-, *s*- or *t*-butyllithium. Basically, it is possible to use a dilithium compound such as dilithium naphthalene or dilithium stilbene, in which case blocks having two living chain ends are obtained. The initiator is normally used in an amount of from 0.0005 to 1 g of lithium per 100 g of monomer.

The polymerization may be carried out in the presence of conventional additives such as chain stoppers, e.g. 1,2-propadiene and 1,2-butadiene, and accelerators, e.g. lithium alcoholates. Proton-active substances must be excluded. We prefer to carry out the polymerization under a blanket of inert gas such as nitrogen or argon, it being necessary to exclude oxygen. The polymerization temperature is generally from 0° to 120°C.

The molecular weight of block B may vary within wide limits ranging from 1,000 to 500,000. Preferably it is from 10,000 to 200,000.

In stage (b) of the process, methyl methacrylate is added to the living chain end or ends of block B in an amount of from 0.5 to 10% and preferably from 1 to 5% by weight of the block B. This polymerization is conveniently carried out in situ. Short polymethyl methacrylate chains are added to block B in this stage with the formation

of ester end groups bearing a "living" CH₂ group. The reaction competing with the polymerization of the methyl methacrylate, namely the reaction of the ester group of the methyl methacrylate with the living chain end of block B with chain termination, may be ignored in most cases. It may be completely suppressed if a small amount of 1,1-diphenyl ethylene or α -methylstyrene is added, preferably in a 75 molar ratio to the initiator of about 1:1. Another way of achieving this end is to add a polar solvent or to lower the polymerization temperature. The addition polymerization of a small amount of methyl methacrylate produces no marked change in the properties and molecular weight of block B.

Independently of the preparation of block B, block A is made in a separate reaction vessel. Block A is a homopolymer of one or more alkylene oxides or a block copolymer of one or more alkylene oxides with one or more vinyl aromatic and/or diene monomers. Preferably polyethylene oxide or polypropylene oxide is used. To achieve special effects it is possible to use block copolymers of the general formula A'C or A'CA', where A' is a polyalkylene oxide block and C may be polystyrene, polybutadiene or a copolymer of butadiene and styrene. The blocks A must exhibit at least one living chain end having an alkali metal alcoholate group. They may be made in known manner by homopolymerization or block copolymerization of the appropriate monomer(s) using an organosodium or organopotassium compound as initiator in a preferably polar organic solvent. Preferred initiators are addition compounds of sodium and potassium with α -methylstyrene, naphthalene, diphenyl, stilbene or other fused ring systems. The said initiators have a difunctional action and give blocks A having two living chain ends. Monofunctional initiators are for example cumyl potassium, phenyl potassium and benzyl potassium. The initiator is generally used in an amount of from 0.001 to 0.5% by weight based on the monomer(s). Particularly suitable solvents are ethers such as diethyl ether, anisole, tetrahydrofuran and dioxane. Alternatively and particularly when monofunctional initiators are being used, polymerization may be carried out in non-polar hydrocarbon solvents. The polymerization temperature is generally from -120° to +70°C and preferably from -80° to +60°C.

The method of producing block copolymers A'C and A'CA' is described for example in U.S. Patent 3,050,511 or Our co-pending U.K. Patent Application number 29227/73 (Specification No. 1 425 870). The molecular weight of block A is generally

from 1,000 to 500,000 and preferably from 5,000 to 100,000.

- The blocks A have at least one living alkali metal alcoholate end group. When block A reacts with block B, it is this alkali metal alcoholate group which reacts with at least one ester group of the methyl methacrylate end group of block B with the elimination of alkali metal methoxide.
- 10 The combination of blocks A and B is conveniently effected by bringing the two solutions together, preferably at temperatures of from -50° to $+100^{\circ}\text{C}$. Blocks A and B may react with each other in a variety of ways: there may result two-blocks AB, three blocks BAB or ABA and also branched and crosslinked reaction products according to whether the blocks used have one or two living chain ends. Another possibility is that the living alkali metal alcoholate group of block A attacks more than one ester group of a polymethyl methacrylate grouping of one block B. This is particularly likely to occur when the number of blocks A is larger than the number of blocks B during the reaction. In this way, there are produced graft copolymers in which a number of side chains A are attached by reaction to a backbone chain B.

Following the reaction of the blocks, the living chain ends are conveniently stopped by adding proton-active substances such as organic acids, e.g. acetic acid. The block copolymers may be precipitated from solution with petroleum ether, where the alkylene oxide content is high, or with alcohol or water, where the alkylene oxide content is low. The block copolymer is then isolated by filtration or by distillation of the solvent.

The polymer block B has a hydrophobic character, whereas block A is hydrophilic. By varying the ratio of block A to block B it is possible to vary the combination of hydrophilic and hydrophobic properties in the block copolymers of the invention in a controlled manner. This gives rise to a variety of applications.

The block copolymers may be used as blending components for a number of plastics materials. If monomeric organic compounds are polymerized in the presence of the block copolymers containing diene polymers, grafting at the double bonds of the diene block may occur. In such polymer blends or graft polymers the hydrophilic polyalkylene oxide segments prevent static electrification. This advantage may be utilized, for example, when modifying styrene polymers in order to render them antistatic and also impact-resistant, in which case the antistatic agent is present as a polymeric component and thus cannot migrate or be extracted. Of particular advantage is the low glass temperature of the

diene polymer blocks B having low 1,2-vinyl content, and such block copolymers are elastomeric within a wide temperature range.

After chain termination, the block copolymers have hydroxy groups at the chain ends. These enable polycondensation reactions to be carried out with difunctional reactants so as to form polyurethanes for example.

Due to their high water absorptive capacity, the block copolymers are suitable for use as coating materials for non-woven fabrics. They may also be used as adhesive primers in bonding procedures or they may be used for blending with plastics to make the latter compatible with each other. The combination of hydrophilic and hydrophobic properties makes them suitable for use as surfactants, protective colloids and emulsifiers.

The invention is further illustrated by the following Examples.

EXAMPLE 1

(a) 1,500 ml of toluene distilled over butyl lithium, 30 ml of a 0.15M solution of butyl lithium in hexane and 325 g of butadiene distilled over butyl lithium are mixed together. The butadiene is polymerized at from 50° to 60°C , a 100% conversion being achieved after about 2 to 3 hours. The molecular weight of the resulting block B is found to be 95,000 by viscosity methods. The resulting polybutadiene contains 11.1% of units of 1,2-vinyl structure.

(b) To this solution there are added 1ml of 1,1-diphenyl ethylene and 10 ml of methyl methacrylate at room temperature.

(c) In a separate polymerization vessel, 1,500 ml of tetrahydrofuran distilled over α -methylstyrene dipotassium, 30 ml of a 0.5M solution of tetrameric α -methylstyrene dipotassium in tetrahydrofuran and 355 g of ethylene oxide distilled over butyl lithium are mixed together. Ethylene oxide is polymerized at from 30° to 40°C , a 100% conversion being achieved after approximately 4-5 hours. The molecular weight of the resulting block A is found to be 36,000 by viscosity methods.

(d) The contents of the two reaction vessels are combined and the mixture is stirred for about 4 hours at room temperature.

The mean molecular weight of the resulting block copolymer is found to be 175,000. It contains polyethylene oxide as block A and polybutadiene as block B.

EXAMPLE 2

(a) A mixture is formed from 1,500 ml of toluene, 182 g of styrene, 325 g of butadiene and 30 ml of a 0.15M solution of butyl lithium. Polymerization produces a polymer block B having a molecular weight of about 145,000.

(b) To this solution there are added 1 ml of 1,1-diphenyl ethylene and 20 ml of methyl methacrylate at room temperature.

(c) In a separate vessel there are mixed 1,500 ml of tetrahydrofuran, 440 g of ethylene oxide and 20 ml of a 0.5M solution of tetrameric α -methylstyrene dipotassium. Polymerization gives a polymer block A having an average molecular weight of 85,000.

(d) The contents of the two vessels are combined. The resulting block copolymer has an average molecular weight of 205,000. It contains polymer blocks A of polyethylene oxide and polymer blocks B themselves consisting of a polystyrene block and a polybutadiene block showing gradual transitions between the blocks.

EXAMPLE 3

(a) In a first vessel there are mixed 1,500 ml of toluene, 455 g of styrene and 20 ml of a 0.15M solution of butyl lithium. Polymerization gives a polymer block B having an average molecular weight of 170,000.

(b) To this solution there are added 1 ml of 1,1-diphenyl ethylene and 20 ml of methyl methacrylate.

(c) In a second vessel there are mixed 2,500 ml of tetrahydrofuran, 750 g of ethylene oxide and 35 ml of a 0.5M solution of tetrameric α -methylstyrene dipotassium. Polymerization gives a polymer block A having an average molecular weight of 80,000.

(d) The two solutions are combined, and the block copolymer resulting from the reaction has an average molecular weight of 295,000. It contains polymer blocks A of polyethylene oxide and polymer blocks B of polystyrene.

EXAMPLE 4

(a) 1,500 ml of toluene distilled over butyl lithium, 30 ml of a 0.5M solution of butyl lithium in hexane and 325 g of butadiene distilled over butyl lithium are mixed and reacted at 60°C. The molecular weight of the resulting polybutadiene (block) B is found to be 105,000.

(b) To this "living" solution of polymer there are added 5 ml of α -methylstyrene and 20 ml of methyl methacrylate at 0°C.

(c) In a separate polymerization vessel there are mixed 1,500 ml of toluene (distilled over butyl lithium) and 20 ml of an approx. 0.3M suspension of cumyl potassium in heptane. With vigorous stirring there are added 150 g of styrene at 40°C, polymerization being effected with 100% conversion after 1 hour. A small portion of the solution is removed for analysis purposes and the molecular weight is found to be 35,000.

To this living solution of polystyrene there are added 300 ml of ethylene oxide distilled

over butyl lithium and polymerization is continued to completion at from 40° to 50°C within a few hours. The molecular weight is found to be about 95,000. There is formed a two-block polymer AC of polyethylene oxide and polystyrene containing 66.5% by weight of ethylene oxide.

(d) The contents of the two vessels are combined and stirred for 2 hours at 50°C. The resulting block copolymer of butadiene, styrene and ethylene oxide has an average molecular weight of 185,000.

WHAT WE CLAIM IS:—

1. A process for the manufacture of a block or graft copolymer of one or more polyalkylene oxide blocks A and one or more vinylaromatic polymer and/or diene polymer blocks B, in which

(a) one or more vinylaromatic monomers and/or diene monomers are polymerized in a non-polar hydrocarbon solvent to form a block B using an organolithium compound as initiator,

(b) methyl methacrylate is added to the living chain ends of the polymer block B in an amount of from 0.5 to 10% w/w of block B.

(c) a polymer block A is separately made by homopolymerization of one or more alkylene oxides or block copolymerization of one or more alkylene oxides with one or more vinylaromatic monomers and/or diene monomers using an organo-sodium or organopotassium compound as initiator in an organic solvent and

(d) block A is finally added to block B with the reaction of at least one living alkali metal alcoholate end group of block A with at least one ester group of block B with the elimination of alkali metal methoxide.

2. A process as claimed in claim 1, wherein in step (a) one or more monomers selected from styrene, nuclear-substituted styrenes, α -methylstyrene, butadiene and isoprene are polymerised in a non-polar aromatic solvent free from or containing up to 10% by weight, based on the total solution, of polar solvent to form a block B having a molecular weight of from 1,000 to 500,000.

3. A process as claimed in claim 1 or 2 wherein in step (b) methylmethacrylate is added to the living chain ends of the block B in an amount of from 1 to 5% w/w of block B.

4. A process as claimed in any of claims 1 to 3 wherein in step (b) 1,1-diphenylethylene or α -methylstyrene is added in a molar amount comparable with that of the methyl methacrylate.

5. A process as claimed in any of claims 1 to 4 wherein step (c) is performed in a

polar organic solvent using a difunctional organo - sodium or organo - potassium initiator to form a block A having a molecular weight of from 1,000 to 500,000.

5 6. A process as claimed in any of claims 1 to 5, wherein step (d) is performed at a temperature of from -50 to $+100^{\circ}\text{C}$.

7. A process as claimed in any of claims 1 to 6 wherein the living chain ends are 10 stopped, following reaction of the blocks, by addition of an organic acid.

8. A process for the manufacture of a block or graft copolymer of one or more polyalkylene oxide blocks A and one or 15 more vinylaromatic polymer and/or diene polymer blocks B substantially as described in any of the foregoing Examples.

9. Block or graft copolymers when

manufactured by a process in any of claims 1 to 8.

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10. Block copolymers of the formula BA or BAB, wherein block A is a polyalkylene oxide and block B is a diene polymer, in which less than 60% of the diene units are of the 1,2-vinyl structure and the blocks 25 are linked by one or more methyl methacrylate units.

11. Block copolymers as claimed in claim 10 in which less than 15% of the diene units are of the 1,2-vinyl structure. 30

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